[pex42] Critical aggregation of bilayers

As it turns out, the critical aggregation of amphiphile molecules into planar bilayers is more akin to the the CMC of spherical micelles [pex40] than to the CMC of cylindrical micelles [pex41]. Curvature does not come into play in this case. The average change in free energy of an amphiphile when it joins an aggregation depends on the size of the bilayer via a characteristic perimeter effect,

$$\epsilon_m = \epsilon_\infty + \frac{\alpha k_B T}{\sqrt{m}}, \tag{1}$$

where α is an effective edge energy in units of the thermal energy. As in [pex40] we write

$$X_m = m \exp\left(\frac{m(\mu - \epsilon_m)}{k_B T}\right), \quad m = 1, 2, \ldots \tag{2}$$

(a) Infer from expressions (1) and (2) the relation

$$X_m = m\Big[X_1 e^{\alpha}\Big]^m e^{-\alpha\sqrt{m}}, \tag{3}$$

by eliminating the chemical potential μ. This result indicates that large disks with open perimeters are exponentially suppressed.

(b) Compute the concentration of size-m bilayers, X_m, and the total concentration of amphiphiles, $\phi \doteq \sum_m X_m$, as functions of the variable α and the parameter X_1 (the concentration of amphiphiles in solution). Use a cut-off m_{max} in the sum large enough that its effect on the results is negligible. The concentration of aggregated amphiphiles is $X_{\text{agg}} \doteq \phi - X_1$. Plot (parametrically) curves of X_1 and X_{agg} versus ϕ. Use several values of the energy constant in the range $1 < \alpha < 7$. For each choice of α, zoom into the range of ϕ where interesting physical phenomena take place such as (more or less abrupt) changes in the concentrations of free and aggregated amphiphiles.

(c) Identify data points for the critical aggregation concentration (CAC) of planar micelles. Try to fit these data points to a model expression for $\phi_c(\alpha)$.

[adapted from Jones 2002]

Solution: